ERDC WQTN-PD-15
April 2004

Phosphorus Forms and Export from Four Sub-watersheds in the Upper Eau Galle River Basin Exhibiting Differing Land-Use Practices

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PURPOSE: The purpose of this research was to quantify biologically labile and refractory phosphorus constituents, transformations, and export from four sub-watersheds in the Upper Eau Galle River basin exhibiting both differing percentages of land-use practice and differing spatial distribution of land uses within the watershed. Land-use practices included livestock containment areas, agricultural fields, grass hay or meadows, CRP, and woodlots. Information from this demonstration will be important in calibrating and improving watershed models to forecast the impacts of land-use practice and BMP's (Best Management Practices) on water quality in Corps receiving waters.

BACKGROUND: Land-use practice undoubtedly plays an important role in the magnitude and extent of phosphorus (P) export from watersheds. It is, therefore, critical to identify the degree of soil phosphorus fertility management of different land-use practices in relation to runoff susceptibility and loss of P to receiving waters in order to more accurately implement BMP's (Best Management Practices) to reduce P loading (Lemunyon and Gilbert 1993, Sharpley et al. 1993, Sharpley 1995, Bundy et al. 2001). To improve prediction of watershed loading impacts on receiving water eutrophication, information is also needed on the composition and biological availability of particulate as well as soluble P loads in the runoff as impacted by differing land-use practices in the watershed (Sharpley et al. 1991, 1992; James et al. 2002; James et al., in publication (b)). This demonstration evaluated particulate and soluble P forms in the runoff of four small sub-watersheds in the Eau Galle River basin, Wisconsin. Land-use practices in the sub-watersheds ranged from livestock and corn production to woodland and grasslands. Objectives were to evaluate the impacts of the land-use mosaic on vulnerability to P loss, magnitude of P loading, and biological availability of P loads to receiving tributaries.

METHODS: The Upper Eau Galle River basin drains a 123.3-km^2 watershed above Eau Galle Reservoir, a Corps impoundment located in west-central Wisconsin (Figure 1). Agricultural land uses in the watershed are dominated by annual and perennial crop production (i.e., corn, oats, alfalfa, grass hay, soy beans), pasture, and livestock dairy production. Other land uses include CRP (Conservation Reserve Program) and wooded areas. Other than one small town (Woodville; population = 1100) located near the approximate center of the watershed, the residential distribution is sparse and rural. Overall, agricultural land uses comprise 93 percent of the watershed area; versus 2 percent for urban/residential settings and 5 percent for woodlands.

Phosphorus forms in runoff and export were examined at three sub-watersheds located in the Upper Eau Galle River basin and at one sub-watershed at an adjacent watershed (French Creek) during the summer of 2003 (Figure 1). Eight-Mile Run, which drains a 264-ha watershed, is divided into nearly two equal halves by an elevated railroad bed. Land use in the Upper Eight-Mile Run (i.e., above or north of the railroad bed) was dominated by meadows, grass hay, CRP (Conservation Reserve

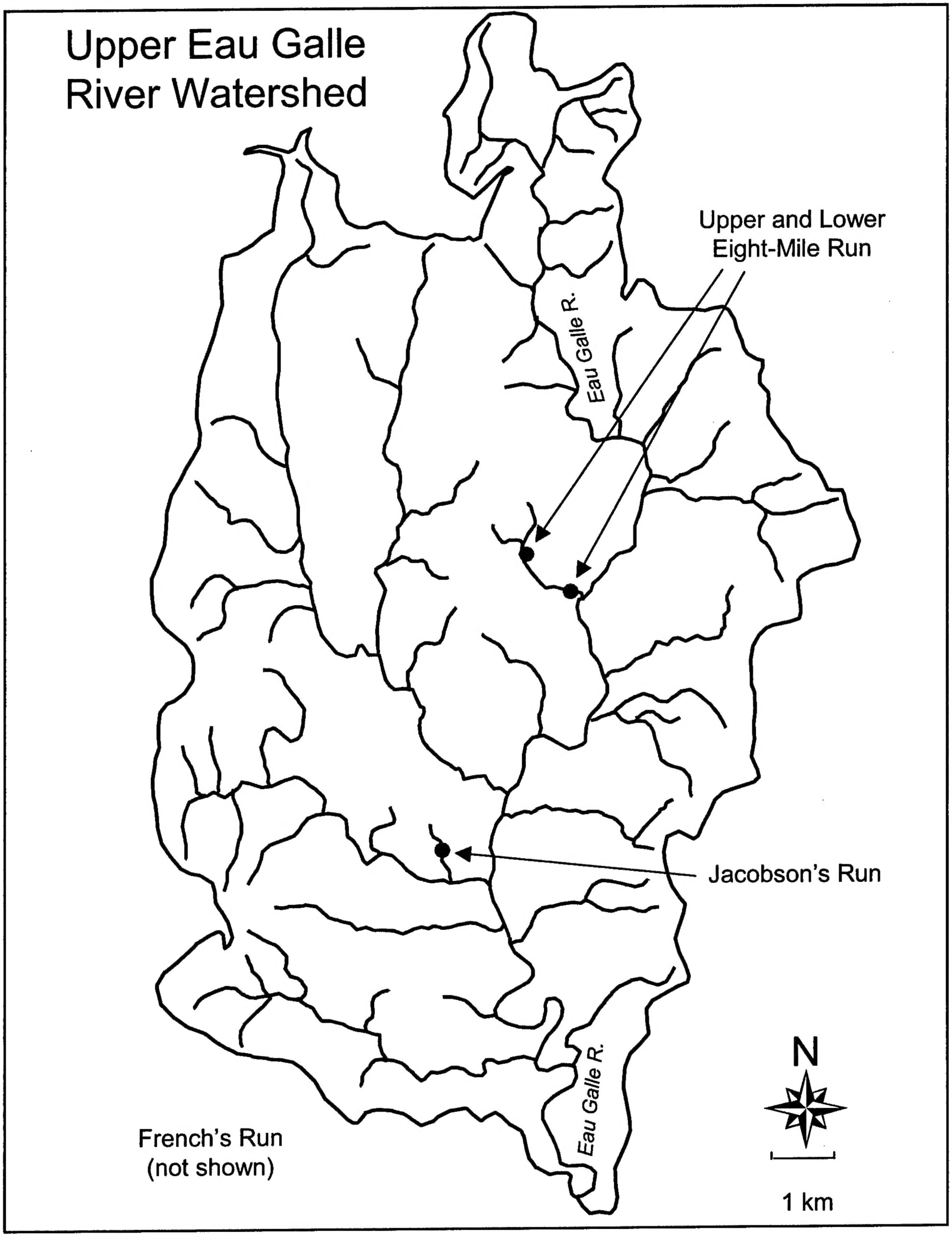


Figure 1. Sampling station locations for Upper and Lower Eight-Mile Run and Jacobson's Run in the Upper Eau Galle River (UEGR) watershed. French's Run was located immediately south of the UEGR

Program), and woodlots (Table 1 and Figure 2). Only a small fraction of its watershed was used for agricultural purposes (primarily corn and alfalfa) and fields were located in the northern headwaters area. In the lower portion of the Eight-Mile Run watershed (i.e., south of the railroad cut), land use was dominated by intensive agricultural row copping (primarily corn; Table 1). Although livestock (dairy cows) containment areas occupied only 6 percent of the watershed, they were located near its base (i.e., before the run enters the Upper Eau Galle River) and adjacent to Eight-Mile Run (Figure 3). The livestock area included two barnyard feedlots and several fenced forage areas that lay on either side of the tributary (Figure 2). Livestock were free to trample the banks and walk in the run during the summer. No vegetated buffer strips occurred along the tributary in the livestock area and grazed forage areas and barnyard feedlots extended directly to the tributary's banks. Dairy cows (50 to 100 head) occupied this area for several months during the summer.

Table 1
Watershed Area and Land Use Percentages for the Various Watersheds[1]

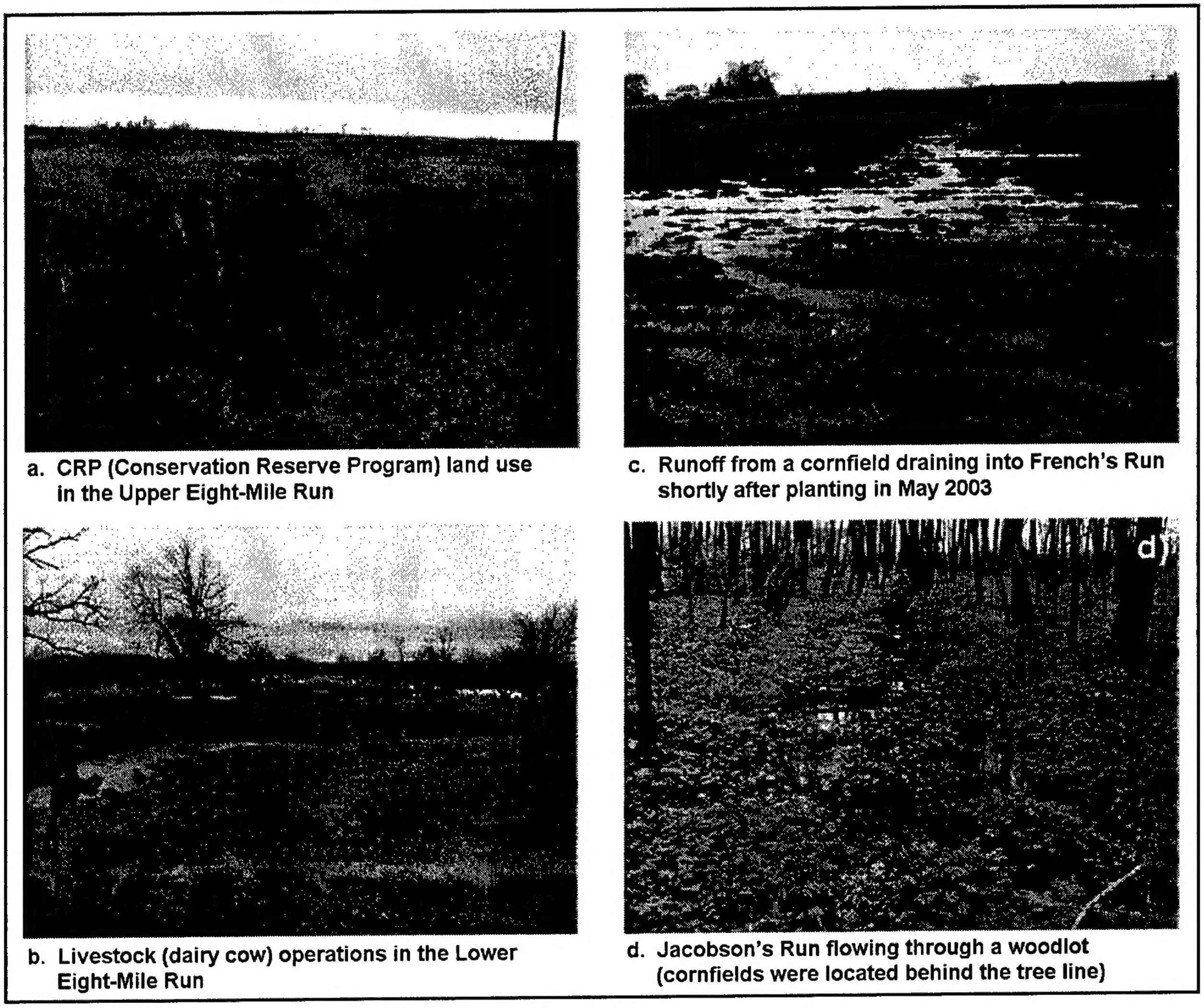
Land Use	Upper Eight-Mile Run	Lower Eight-Mile Run	French's Run	Jacobson's Run
Total area (ha)	114.1	150.0	5.2	7.0
Livestock containment (%)	1	7	0	0
Agricultural fields (%)	8	42	74	36
CRP, grass hay, meadow (%)	58	31	26	18
Woodlots (%)	33	20	0	46

[1] The Upper Eight-Mile Run watershed is defined as the areas above the tributary monitoring station located near the railroad bed (Figure 3). The Lower Eight-Mile Run watershed is defined as that area located between the mouth of the tributary and the Upper Eight-Mile Run sampling station.

The French's Run study site was located in the headwaters of French Creek watershed, which is adjacent to and just south of the Upper Eau Galle River basin (Figure 1). The only defined channels in French's Run were ditches located on either side of two roads that bisected the watershed (Figure 2). Land use in the watershed was dominated by corn production during the study period (Table 1) and flows during storm events occurred as overland runoff from the field that drained directly into the ditches and a culvert that passed under a road (James et al., in publication (c)). Runoff was exacerbated by contouring crop rows parallel to the slope of the field to promote better field drainage (Figure 2).

Land use in the Jacobson's Run watershed was dominated by a woodlot (Figure 3). Agricultural fields also comprised a large portion of its area (Table 1). The run had several defined natural channels located in the densely wooded area that were fed by natural springs (Figures 2 and 3). However, spring flow was very low and represented a minor to negligible contribution to flow during storms. Ditches along roadsides also contributed flow during storm events. Drainage to the ditches originated from the adjacent roads and the grass land-use areas (primarily CRP). No defined channels or drainage runs occurred in the agricultural field (corn production) located above the woodlot and the field was contoured perpendicular to the slope to minimize overland runoff.

For Eight-Mile Run, an automated water sampling and flow gauging station was established below the railroad bed to monitor loading from the upper portion of the watershed. Another sampling and gauging station was established in the lower portion of the watershed near the run's confluence with the Upper Eau Galle River (Figure 3). Stage height was recorded at 15-min intervals using an



a. CRP (Conservation Reserve Program) land use in the Upper Eight-Mile Run

b. Livestock (dairy cow) operations in the Lower Eight-Mile Run

c. Runoff from a cornfield draining into French's Run shortly after planting in May 2003

d. Jacobson's Run flowing through a woodlot (cornfields were located behind the tree line)

Figure 2. Examples of dominant land-use practices adjacent to tributaries of the various watersheds

ISCO 6700 sampler with a 730 bubbler module (ISCO Incorporated, Lincoln, Nebraska). A stage-discharge relationship was determined over a variety of flow regimes to convert stage height to volumetric flow. For the Jacobson's and French's Run watersheds, all runoff drained into culverts located underneath local roads. Thus, instantaneous velocity and stage height were measured in the culverts at 15-min intervals using an ISCO 4150 area-velocity sensor. Precipitation gauges (Dataloggers; Model S-162), monitored rainfall over 15-min intervals. Flows and precipitation were monitored between May and August 2003.

At all stream sampling locations, water samples were collected at short time intervals (15-30 min) with automated sampling equipment (ISCO 6700 samplers), and composited into daily, flow-weighted samples for chemical analysis. In the laboratory, a portion was filtered through a 0.45-µm filter for soluble constituent determination. Soluble reactive P (SRP) was analyzed using automated analytical techniques (Lachat QuikChem® Autoanalyzer, Hach Company, Lachat Div., Loveland,

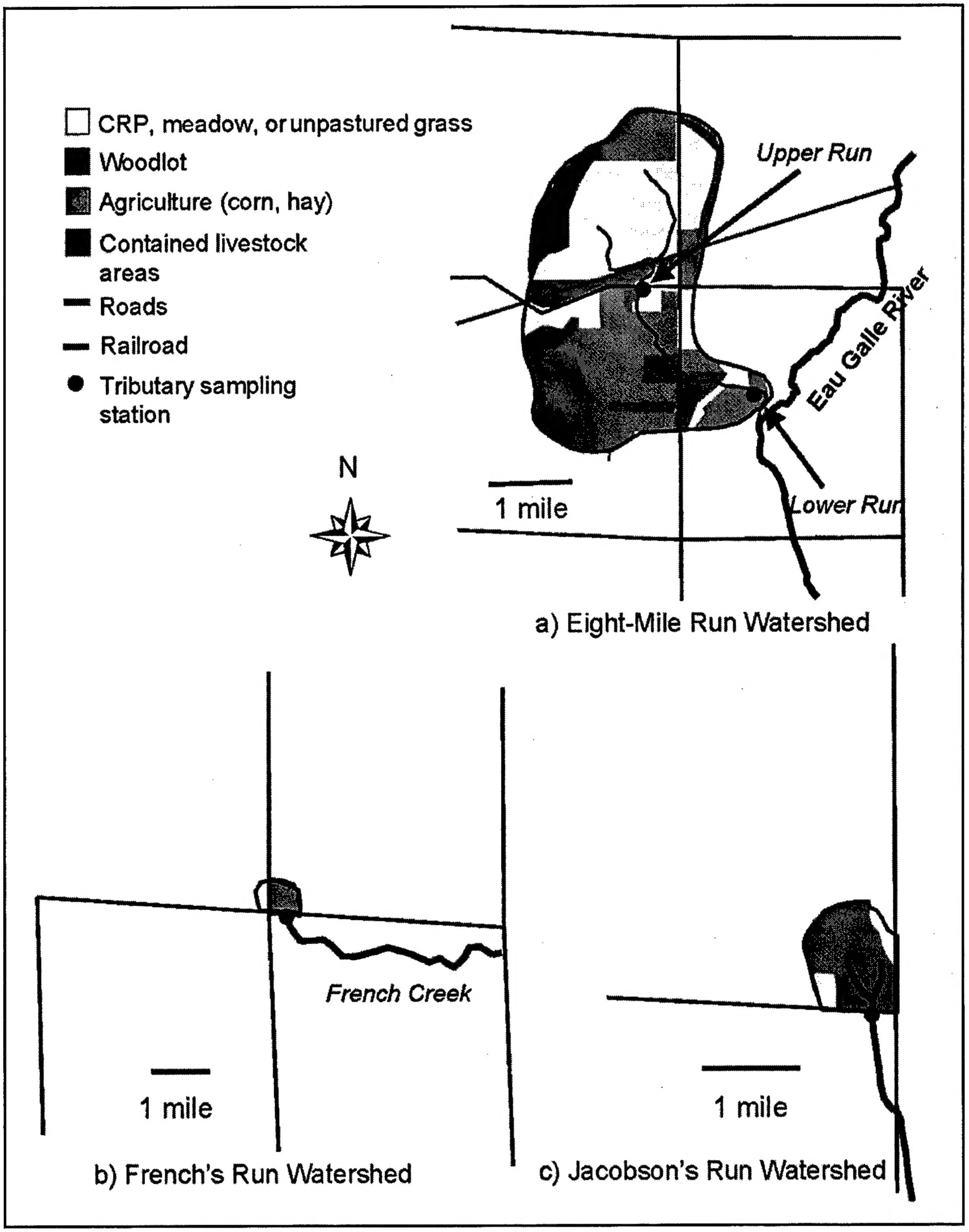


Figure 3. Land-use coverage, locations of roads and railways, and tributary sampling locations

Colorado). Total and total soluble P were analyzed colorimetrically using Lachat QuikChem® procedures following digestion with alkaline potassium persulfate according to Ameel et al. (1993). For particulate components, sample aliquots were retained on glass fiber filters (Gelman Metricel; 2 µ nominal pore size). For total suspended solids (TSS), particulate material was dried at 105 °C to a constant weight (American Public Health Association (APHA) 1998). Additional sample was filtered onto glass fiber filters for sequential fractionation of particulate phosphorus. P fractionation was conducted according to Hieltjes and Lijklema (1980) and Nürnberg (1988) for the determination of ammonium-chloride-extractable particulate P (PP; loosely bound P), bicarbonate-dithionite-extractable PP (i.e., iron-bound PP), sodium hydroxide-extractable P (i.e., aluminum-bound PP), and hydrochloric acid-extractable P (i.e., calcium-bound PP). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable PP (Psenner and Puckso 1988). Labile particulate organic/polyphosphate PP was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. PP remaining on the filter after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid for determination of refractory organic PP. Each extraction was filtered through a 0.45-µm filter, adjusted to pH 7, and analyzed for SRP using the ascorbic acid method (APHA 1998). Table 2 describes operationally defined PP fractions measured in this study and biological availability.

Table 2
Operationally Defined Phosphorus Fractions [1]

Variable	Extractant	Biological Availability and Susceptibility to Recycling Pathways
Loosely bound P	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes
Aluminum-bound P	0.1 N sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial
Calcium-bound P	0.5 N hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial
Labile organic/ polyphosphate P	Persulfate digestion of the NaOH extraction	Biologically labile; polyphosphates are available for biological uptake. Also recycled via bacterial mineralization and surplus storage in cells
Refractory organic P	Persulfate digestion of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial

[1] Labile = Susceptible to recycling pathways or direct availability to the biota; Refractory = Low biological availability and susceptible to burial.

To measure P sorption characteristics of TSS loads, the remaining composited sample was centrifuged at 500 g and decanted to separate particulate from soluble phases. TSS aliquots (~500 mg/L dry weight equivalent) were subjected to a series of SRP (potassium dihydrogen phosphate; KH_2PO_4 as SRP) standards ranging from 0 to 1.0 mg/L (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg/L) for examination of P adsorption and desorption over a 24-hr period. Untreated tap water from the laboratory was used as the water medium because it was phosphate-free and exhibited cationic strength, conductivity, and pH very similar to that of surface water from the Eau Galle River. Chloroform (0.1 percent) was added to inhibit biological activity (Detenbeck and Brezonik 1991). The sediment systems, containing TSS, tap water, and known concentrations of SRP, were shaken uniformly for 24 hr and then sampled and analyzed for SRP (APHA 1998). The sediment systems were maintained under oxic conditions at a pH of ~8.0 to 8.3 and a temperature of ~20 °C .

The change in SRP mass (i.e., initial SRP - final SRP; mg) over the 24-hr period was divided by the dry mass equivalent of wet sediment used in the experiment to determine the quantity of P desorbed

or adsorbed (mg P kg^{-1} sediment). These data were plotted as a function of the equilibrium SRP concentration after 24 hr of incubation to determine the linear adsorption coefficient (K_d; L kg^{-1}), the equilibrium P concentration (EPC; mg P L^{-1}; the point where net sorption is zero), and the native adsorbed P (S_o; mg P kg^{-1} sediment; initial P adsorbed to the sediment). The Kd and S_o were calculated via regression analysis as the slope and the y-intercept, respectively, from linear relationships between final SRP concentrations and the quantity of P sorbed at low equilibrium concentrations (Pant and Reddy 2001). The EPC was calculated as S_o divided by K_d.

Daily constituent loading rates were determined using the software program FLUX (Walker 1996). Constituent loading was calculated either as the product of a flow-weighted average concentration and mean flow over different flow strata or by linear regression analysis of concentration versus flow. Constituent loadings at individual stations were also normalized with respect to the watershed area above each station to estimate export (mass m^{-2} d^{-1}). Average loads and export rates for Lower Eight-Mile Run were calculated as the value determined at the lower station (i.e., the entire watershed) minus the load determined at the upper station.

RESULTS: Precipitation was below average for the summer period (-16.1 cm between April and September for Eau Claire, Wisconsin) as drought conditions occurred between June and September 2003. However, it was near normal for the months of May through July (-2 cm). During that latter period, daily precipitation exceeding 20 mm occurred on four days (Figure 4a). A daily precipitation maximum of 65 mm was observed on 25 June. Numerous smaller precipitation events also occurred during the 3-month period. Peaks in flow were observed in response to precipitation for all monitored tributaries (Figures 4b and 4c).

Daily flow for the May through July study period was similar between Upper and Lower Eight-Mile Run and lower for the smaller French's and Jacobson's Run watershed (Figure 5a). Areal runoff (i.e., mm d^{-1}) was lowest and similar between Upper and Lower Eight-Mile Run. However, it was higher for the wooded Jacobson's Run compared to Eight-Mile Run. French's Run exhibited the highest areal runoff during the study period.

The lower portion of the Eight-Mile Run watershed accounted for nearly all (i.e., 99 percent) of the TSS and total P loading from the entire watershed and exhibited the greatest export rate versus the Upper Run (Figures 5b and 5c). Loadings from the Upper Eight-Mile Run were negligible in comparison to the Lower Run. Over all watersheds, the Upper Eight-Mile Run exhibited the lowest loading and export rates for TSS and total P followed by Jacobson's Run. The highest export rates were observed for French's Run and Lower Eight-Mile Run.

There were distinct differences in the composition of P loads between the watersheds (Figure 6). For Eight-Mile Run, soluble forms of P comprised over 60 percent of the total P load (75 percent for the Upper Run and 64 percent for the Lower Run). Labile PP forms (i.e., loosely bound PP, iron-bound PP, and labile organic/polyphosphate PP) accounted for 13 percent and 20 percent of the total P composition for the Upper and Lower Run, respectively. Thus, biologically labile particulate and soluble P forms collectively accounted for more than 80 percent of the flow-weighted total P composition. Since loads and concentrations were minor from the Upper Run versus the Lower Run,

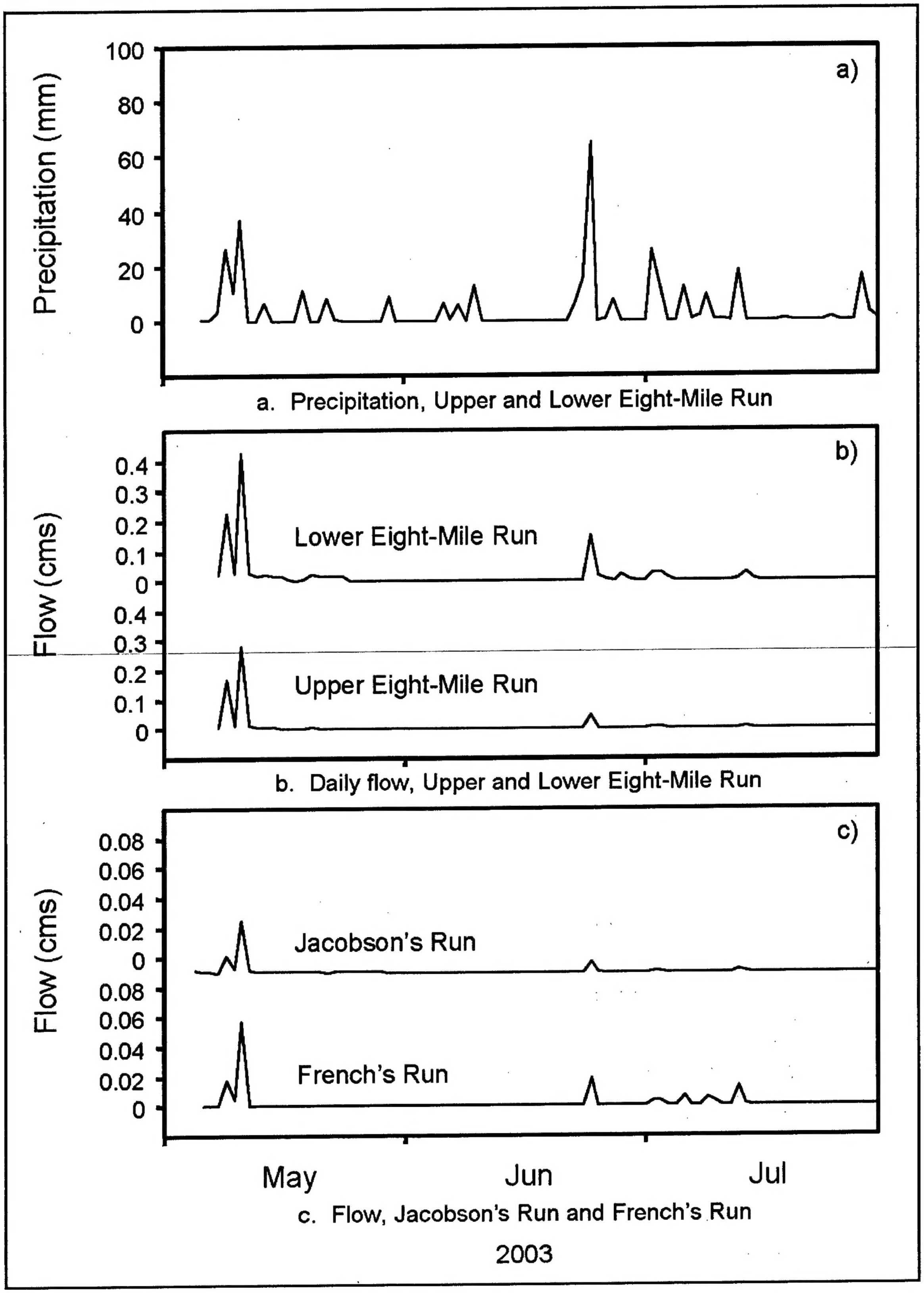


Figure 4. Variations in daily precipitation and daily flow during the summer, 2003

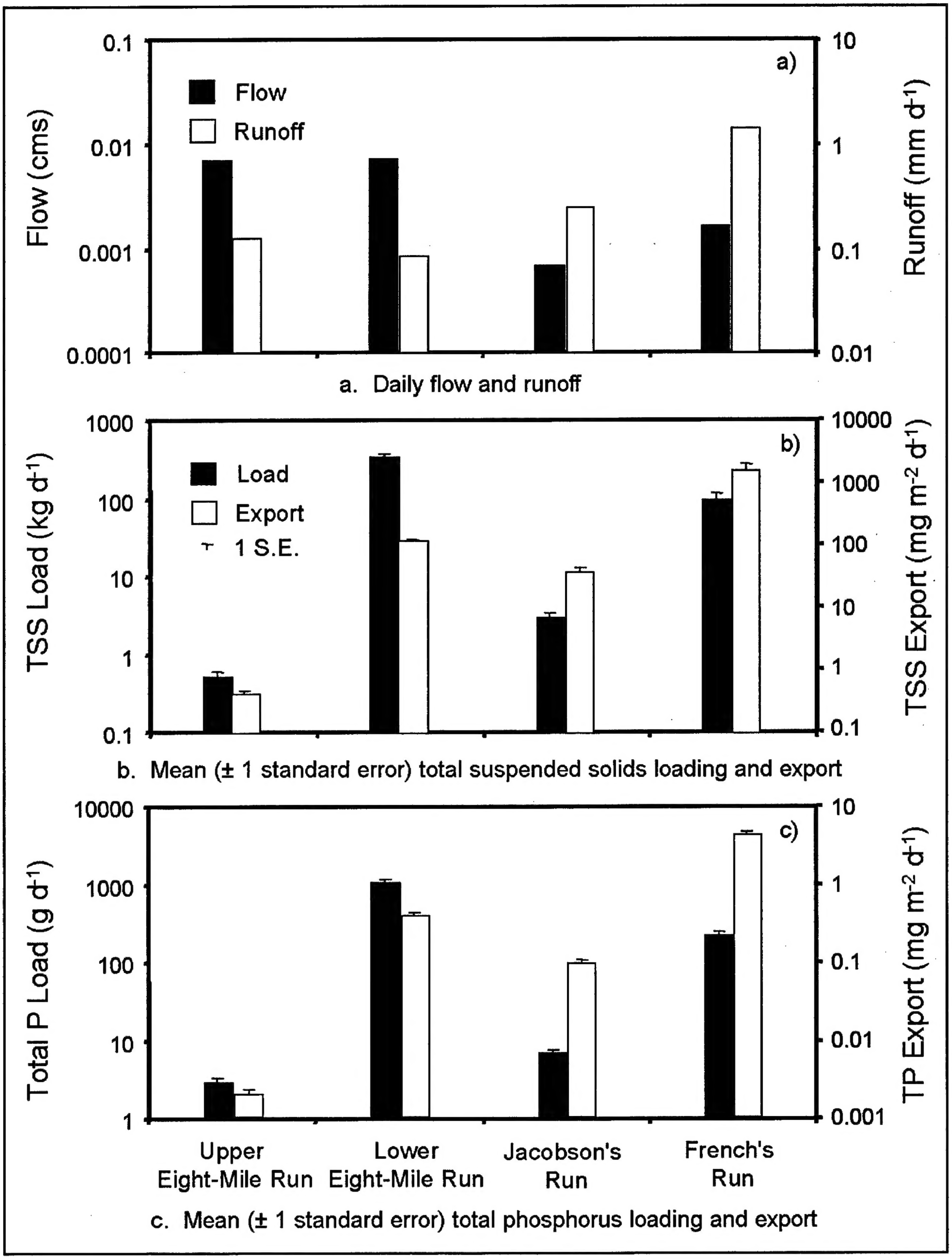


Figure 5. Statistics for the various tributaries (note the logarithmic scales used in each panel)

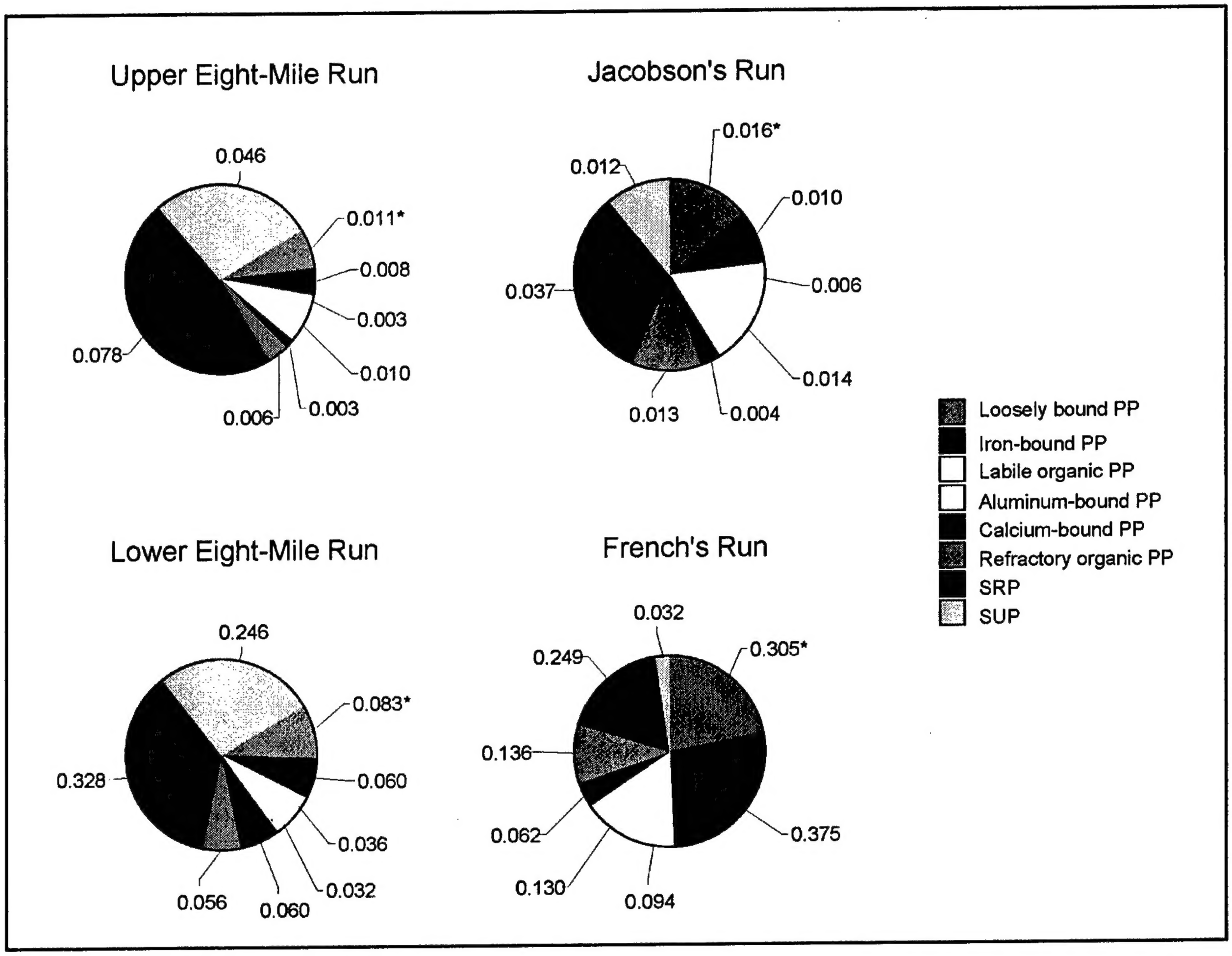


Figure 6. Composition of total phosphorus loads for Upper and Lower Eight-Mile Run, Jacobson's Run, and French's Run. Flow-weighted concentrations (shown next to the leaders) are expressed as mg L^{-1}. PP = particulate phosphorus, SRP = soluble reactive phosphorus, and SUP = soluble unreactive phosphorus. The asterisk denotes the loosely bound PP fraction for each watershed. Other fractions follow the legend in clockwise order starting with the loosely bound PP fraction

it was clear that runoff from land-use practices in the Lower Run was responsible for the high loads of biologically labile P being discharged from the Eight-Mile Run watershed into the Upper Eau Galle River.

In contrast, particulate P forms, versus soluble P, dominated the total P composition of the runoff from French's Run (i.e., 80 percent; Figure 6). The loosely bound and iron-bound PP fractions comprised nearly 90 percent of the labile PP in the runoff. Refractory PP forms (i.e., aluminum-bound, calcium-bound, and refractory organic PP) accounted for only 23 percent of the total P. Overall, labile particulate and soluble forms of P represented 75 percent of the total P in the runoff from this watershed. Similar patterns in P composition were observed for both Eight-Mile and French's Run in summer 2002 (James et al., in publication (c)).

For Jacobson's Run, particulate and soluble P forms each accounted for approximately 50 percent of the total P composition (Figure 6). Most of the soluble P was in the form of SRP. For particulate P, a large percentage was in the form of refractory fractions versus other watersheds. The labile PP fraction was dominated by loosely bound and iron-bound PP.

Mean sorption characteristics of the TSS loads originating from each watershed are shown in Table 3. The mean EPC was lowest for TSS in the runoff from the Upper Eight-Mile Run and Jacobson's Run. In contrast, TSS from the more agriculturally dominated Lower Eight-Mile Run and French's Run exhibited a very high mean EPC, significantly greater than values observed for the other watersheds (ANOVA, $p < 0.05$; SAS Institute (1994)). Lower Eight-Mile Run and French's Run also exhibited the highest mean S_o. TSS in the runoff of Jacobson's Run exhibited the lowest mean S_o of the four sub-watersheds, while mean S_o for particulate runoff from the Upper Eight-Mile Run was moderate relative to the other watersheds. There were also significant positive linear relationships between S_o and EPC when data from all watersheds were combined (SAS Institute 1994; Figure 7), suggesting possible links between the concentration of P initially adsorbed onto TSS and the EPC. The greatest S_o and EPC values were associated with TSS in the runoff from Lower Eight-Mile Run and French's Run, while Jacobson's Run and Upper Eight-Mile Run exhibited lower values for these variables (Figure 7). Mean K_d was similar between the four sites (Table 3).

Table 3
Mean[1] EPC,[2] K_d,[3] and S_o[4] for Total Suspended Solids Runoff from the Various Watersheds[5]

Watershed	EPC, mg L^{-1}	K_d, kg^{-1}	S_o mg kg^{-1}
Upper Eight-Mile Run (n=5)	0.080 (0.023)[b]	888 (173)[a]	62 (21)[bc]
Lower Eight-Mile Run (n=9)	0.290 (0.024)[a]	645 (80)[ab]	176 (18)[a]
French's Run (n=6)	0.195 (0.030)[a]	502 (78)[ab]	103 (30)[ab]
Jacobson's Run (n=3)	0.066 (0.010)[b]	552 (110)[ab]	37 (90)[c]

[1] One standard error in parentheses.
[2] Equilibrium phosphate concentration.
[3] Linear adsorption coefficient.
[4] Native adsorbed phosphorus.
[5] Different letters between the means represent significant differences at the 5% level or less (ANOVA; SAS Institute 1994).

With the exception of Jacobson's Run, the mean EPC of TSS loads was very similar to the flow-weighted SRP concentration in the tributary runoff (Figure 8). Jacobson's Run exhibited the lowest mean SRP and EPC of the four sub-watersheds; however, the EPC of TSS loads was significantly higher than the flow-weighted SRP concentration (t-test, $p < 0.05$; SAS Institute 1994). For the other watersheds, statistical differences were not observed between flow-weighted SRP concentration and the mean EPC of the TSS in the runoff.

DISCUSSION: There were apparent links between land-use practices in each watershed and differences in the magnitude of constituent areal export, concentration, and the compositional makeup of total P loads. It also appeared that land uses that were immediately adjacent to the various runs examined had the largest impact on loading and P composition for the four tributaries studied. For instance, even though the Jacobson's Run watershed had a high percentage of agricultural land use, TSS and P export was lower compared to the other sub-watersheds that exhibited relatively large areal percentages of agricultural land use. This pattern was likely due to the location in and exposure of most of Jacobson's Run to the woodlot land-use setting. In contrast, there was little to no direct runoff from the agricultural fields located in the upper portion of the watershed. Any runoff

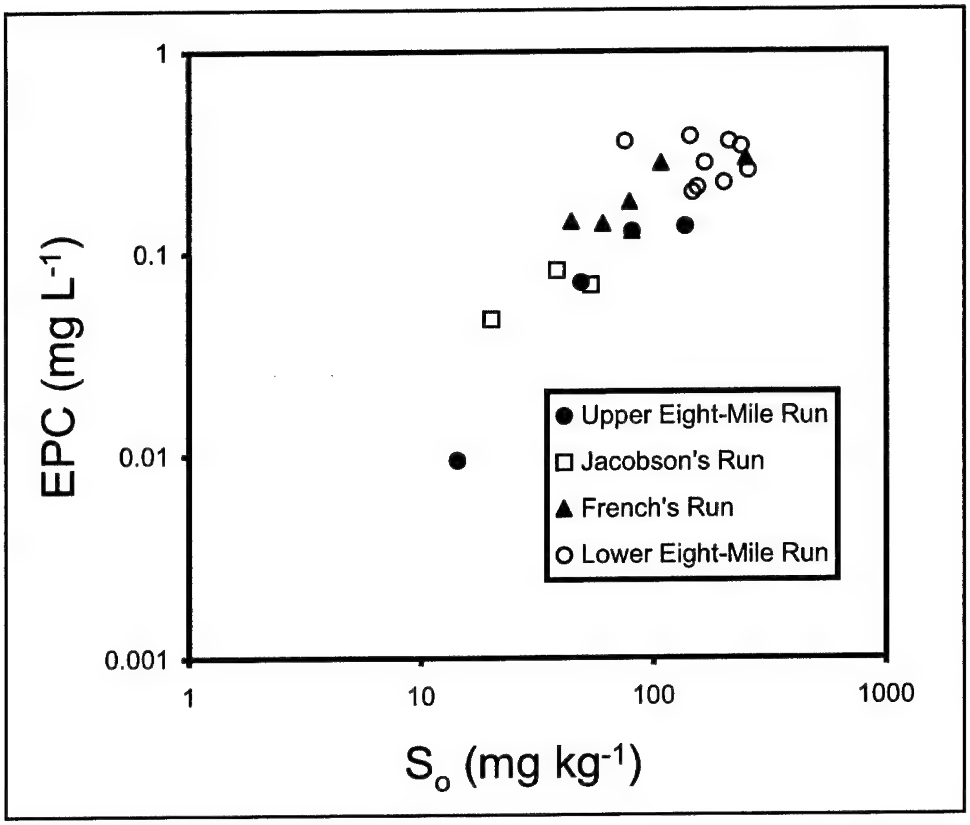


Figure 7. Relationship ($r^2 = 0.71$; $p < 0.05$; linear regression analysis; SAS Institute 1994) between the native adsorbed phosphorus concentration (S_o) and the equilibrium phosphorus concentration (EPC) for total suspended solids in the runoff of various tributaries

that left the agricultural fields also had to move through the woodlot area where it was likely buffered by the forest floor and vegetation before draining into the Run. For French's Run, high runoff and associated high TSS and total P export were attributed to agricultural land use practices of corn production surrounding the tributary, lack of vegetative cover between rows, and poor row contouring, which resulted in field runoff directly to this small tributary. In contrast, very low TSS and P export from the Upper Eight-Mile Run were associated with land-use practices adjacent to this tributary that were dominated by CRP, grass meadows, and grass hay. Agricultural practices in the headwaters of the Upper Eight-Mile Run appeared to have little influence on loading and export characteristics. In the Lower Eight-Mile Run, even though dairy livestock land-use areas occupied only about 6 percent of this portion of the watershed, it appeared this land-use feature had a marked impact on high runoff and export of P-enriched TSS and soluble P relative to the other land-use features located at higher elevations in the watershed. Even though this land use represented a minor portion of the watershed area, it was located immediately adjacent to and surrounding the Lower Eight-Mile Run and occupied approximately 46 percent of the length of the channel. Repeated manure incorporation into soils, diminished vegetative cover due to grazing, and trampling near the tributary banks appeared to have a much greater impact on constituent runoff than the agricultural fields and woodlots located further away from the channel.

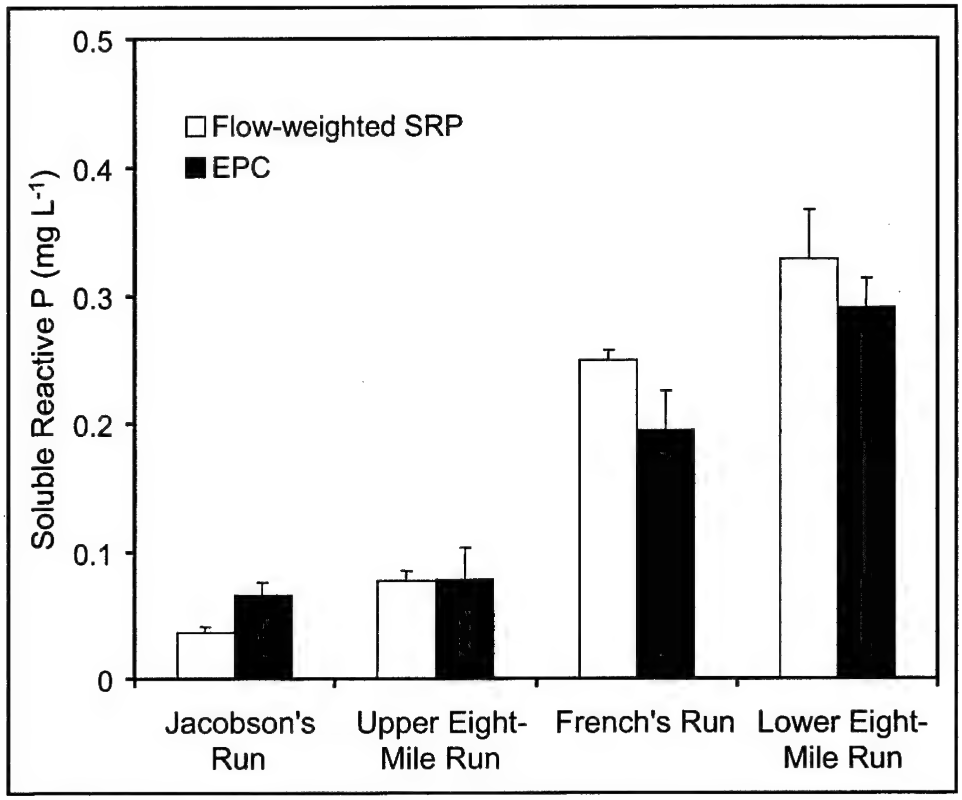


Figure 8. Comparison of mean (vertical lines represent 1 standard error) flow-weighted concentrations of soluble reactive phosphorus (SRP) and the mean equilibrium phosphorus concentration for total suspended solids in the runoff of various tributaries. The mean EPC was significantly greater than the mean flow-weighted SRP concentration for Jacobson's Run ($p < 0.05$; t-test; SAS Institute (1994)). No significant differences were found between these two variables for the other tributaries

Differing land-use practice influences also appeared to be associated with marked differences in the composition of P loads from the various watersheds. In the Upper Eight-Mile Run, relatively low TSS and P loading was associated with the occurrence of predominantly soluble forms of P. Since this portion of the watershed was dominated by various grasslands, particle erosion was probably dampened (Sharpley et al. 1994) and P transformations to soluble forms via desorption and extraction dominated constituent runoff composition (Sharpley 1985). As runoff and loading increased in the lower portion of Eight-Mile Run, P composition was still dominated by soluble P forms. However, higher concentrations of soluble P in the runoff were probably linked to P desorption and extraction from soils containing a high manure content (Sharpley et al. 1994, Nair et al. 1995, Nair et al. 1998, Nair and Graetz 2002) located in the dairy livestock containment areas adjacent to the tributary. Earlier work on watershed soils showed that soils in dairy livestock containment areas of Eight-Mile Run and the Eau Galle watershed exhibited significantly greater organic matter (34 percent ± 8 SD), total P (3215 ppm ± 512 SD), Mehlich-3 P (1615 ppm ± 328 SD), and water-extractable P (49 ppm ± 6 SD) than soils from other land-use areas (James et al., in publication (a)), indicating marked enrichment of readily solubilized phosphorus in the soils by manure incorporation.

The dominance of particulate P forms in the runoff of French's Run indicated particle erosion from exposed and poorly contoured cornfields surrounding the tributary. The biologically labile loosely bound and iron-bound PP fractions accounted for nearly 50 percent of the total P composition and more than 60 percent of the particulate P fraction, suggesting links to soil nutrient management for corn production. The total P composition of loads originating from the Jacobson's Run watershed was also dominated by PP forms. Unlike French's Run, however, refractory and labile PP each accounted for approximately 50 percent of the PP. A relatively larger proportion of refractory PP forms in the P loads from Jacobson's Run may have been due to P associated with leaf litter and organic compost.

The very distinct differences in sorption and equilibrium characteristics of TSS in the runoff were clearly related to differing influences of land-use practice in each watershed. The very high EPC associated with TSS collected in the runoff from the Lower Eight-Mile Run and French's Run suggested that TSS eroding from agricultural and livestock land uses adjacent to the tributary channels was enriched with readily desorbed P and could contribute substantially to high soluble P concentrations in receiving waters under conditions of P disequilibrium between particulate and soluble phases via desorption processes. In contrast, much lower EPC's associated with TSS in the runoff from Upper Eight-Mile Run and Jacobson's Run were likely linked to source soils that had not undergone extensive nutrient management. James et al. (in publication (a)) found that agriculturally managed soils in the Upper Eau Galle River basin exhibited highest crop-available P concentrations (range = 0.12 to 1.6 ppm as Mehlich-3 P) versus lower concentrations for soils located in grass hay (0.10 ppm), CRP (0.08 ppm), and woodlot (0.02 ppm) land uses.

Another important finding in this study was the occurrence of higher S_o (i.e., native adsorbed P) in the runoff from the more agriculturally managed Lower Eight-Mile Run and French's Run versus the less managed Upper Eight-Mile Run and Jacobson's Run. These trends suggested increased binding of P on soil sorption sites for TSS in the runoff of watersheds influenced by agricultural land-use practices and soil nutrient management (Nair and Graetz 2002). In particular, Reddy et al. (1978) found that manure amendments increased the EPC of soils tremendously. Runoff of this TSS could play a very important role in the regulation of soluble P concentrations in receiving waters via equilibrium processes. Other studies have found that eroded soils play an important role in P desorption and soluble P concentrations in receiving waters (Sharpley et al. 1981, Klotz 1988, Pant et al. 2002).

Overall, it appeared that equilibrium processes between TSS and aqueous phases played an important role in regulating SRP concentrations in the runoff from each watershed, as flow-weighted concentrations of SRP were very similar to the EPC of TSS loads. This pattern has important implications for watershed management to reduce P loading to receiving waters, as agricultural soils managed for nutrient fertility would appear to have a negative impact on P loading by regulating SRP concentrations in the runoff and exacerbating high SRP availability to receiving waters. Reducing TSS runoff from P-rich agricultural land uses to reduce soluble P availability would, therefore, be a critical consideration in watershed management.

Finally, the results of this study support the growing body of evidence that location of land-use practices in relation to hydrological sensitivity to direct runoff needs to be considered for better management of watersheds (Gburek and Sharpley 1998; Walter et al. 2000, 2001). For instance, the

land-use mosaic of the Upper Eight-Mile and Jacobson's Run favored much less runoff and export due to the buffering effects of woodlots and grasslands located adjacent to the tributaries versus the other two watersheds that had intensive agricultural land uses next to their tributary channels.

SUMMARY: Study results indicated that both land-use practice and vulnerability to direct P loss into receiving tributaries were important in impacting the magnitude and biological availability of P loads. Agriculturally managed land uses located near tributary channels appeared to be associated with high tributary TSS and P export. Biologically labile forms of particulate and soluble P constituted a large portion of these P loads, and TSS enriched with native adsorbed P interacted with aqueous phases to promote high SRP equilibrium concentrations in the runoff. In contrast, watersheds with land uses consisting of woodlots or various grasslands that were located adjacent to and/or surrounding tributary channels were associated with lower TSS and P export. Native adsorbed P concentrations were lower for TSS in the runoff of these watersheds and the EPC was <0.10 mg L^{-1}. Biologically available forms of P still constituted a large portion of these P loads. However, overall loss of this biologically available P (i.e., export) was much lower from these watersheds compared to the other watersheds exposed directly to agriculturally managed land uses. Thus, the susceptibility of land-use practices to runoff of biologically available forms of P needs to be considered within the context of the land-use mosaic distribution and hydrological susceptibility to receiving tributaries.

ACKNOWLEDGMENTS: The authors gratefully acknowledge L. Pommier of the Eau Galle Aquatic Ecology Laboratory, ERDC, for fractionation and chemical analyses.

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> James, W. F., Eakin, H. L., and Barko, J. W. (2003). "Phosphorus forms and export from sub-watersheds in the Upper Eau Galle River basin exhibiting differing land-use practices," *Water Quality Technical Notes Collection* (ERDC WQTN-PD-15), U.S. Army Engineer Research and Development Center, Vicksburg, MS. *www.wes.army.mil/el/pubs/wqtncont.html*

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